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SUMMARY: SOME RESULTS FROM THE APIOS ATMOSPHERIC DEPOSITION MONITORiNG PROGRAM (1981-1984)

ARB-110-86

APIOS-011-86

November, 1986

Ministry of the Environment
Ontario

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1. INTRODUCTION

This report summarizes some of the main results from the Acidic Precipitation in Ontario Study's (APIOS) deposition monitoring program from 1981 to 1984. The questions addressed include the current levels of deposition of acidifying substances in Ontario, annual and seasonal variations in deposition levels, the relative importance of sulfur and nitrogen oxides as acid-forming substances, the relative importance of wet and dry deposition processes, and the contribution of sources in the United States and Ontario to provincial deposition levels. Some results are also given on the atmospheric deposition of the toxic metals lead and cadmium.

2. THE APIOS WET AND DRY DEPOSITION MONITORING NETWORK

Atmospheric deposition is monitored at more than 50 rural locations in the Province of Ontario. Figure 1(a) shows the sites where sampling is carried out over a 28-day period, while Figure 1(b) shows the sites where daily samples are collected. The 28-day, "cumulative" network is used to determine the long-term wet and dry deposition fields of acidity and related pollutants, such as sulfates and nitrates, as well as various toxic trace metals (such as cadmium and lead). The daily sampling network yields data on sulfur and nitrogen oxide concentrations which can be subjected to meteorological analysis. Air parcel trajectory analysis, for example, can be used to determine the contribution of sources in different compass directions to the atmospheric deposition at a receptor.

Precipitation is sampled using wet-only collectors, an example being shown in Figure 2. Actually, the collector shown on this figure is used in the cumulative network only. For the daily network, a somewhat different design is used, but the principle of operation is the same. The collector vessel is normally covered, but when precipitation falls, a sensor (shown on the protruding arm) activates a motor, which opens the lid. When the precipitation stops, the lid automatically closes. The sample is subsequently removed and sent to the laboratory for chemical analysis.

Dry deposition of pollutants is not monitored directly in the APIOS network - it is inferred from air concentrations. The dry deposition can be estimated for each pollutant if a quantity known as its "deposition velocity" is available. Then the dry deposition rate can be calculated by multiplying the air concentration and deposition velocity. This is possible for many of the pollutants monitored by the APIOS network.

The equipment for monitoring air concentrations uses filter packs. Air is drawn by a vacuum pump over a series of filters (the first designed to remove particulates, and subsequent filters, to trap gaseous sulfur and nitrogen oxides), which are later removed and analysed at the Ministry's laboratory. Figure 3 shows the equipment used in the cumulative air monitoring network, where the air is continuously sampled over a 28-day period. The daily air monitoring stations have somewhat different equipment, but the principle of operation is similar.

1. Colchester*
2. Martin
3. Pt. Stanley*
4. Wilkesport*
5. Alvinston
6. Huron Park
7. Waterloo
8. Palmerston*
9. Shallow Lake*
10. Milton (removed March 1984)
11. Uxbridge*
12. Coldwater
13. Campbellford*
14. Cloyne*
(replacing Kaladar, June 1983)
15. Smith's Falls*
16. Dalhousie Mills*
17. Golden Lake*
18. Wilberforce
19. Whitney
20. Dorset*
21. McKellar*
22. Wattawa*
23. Killarney*
24. Bear Island
25. Gowganda*
26. Azure Lake
(replacing Ramsay, June 1983)
27. Moonbeam*
28. Attawapiskat
(removed February 1984)
29. Winisk
30. Geraldton*
(replacing Nakina, August 1983)
31. Dorion*
32. Quetico Centre*
33. Lac la Croix
34. Experimental Lakes Area
35. Ear Falls*
36. Pickle Lake*
37. Turkey Lake*
38. Moosonee*
(installed October, 1985)
39. Otter Island*
(operated only during "summer" periods)

* indicates both a dry and wet deposition network site

Figure 1(a): The APIOS cumulative precipitation and air monitoring network.

Figure 1(b): The APIOS daily precipitation and air monitoring network

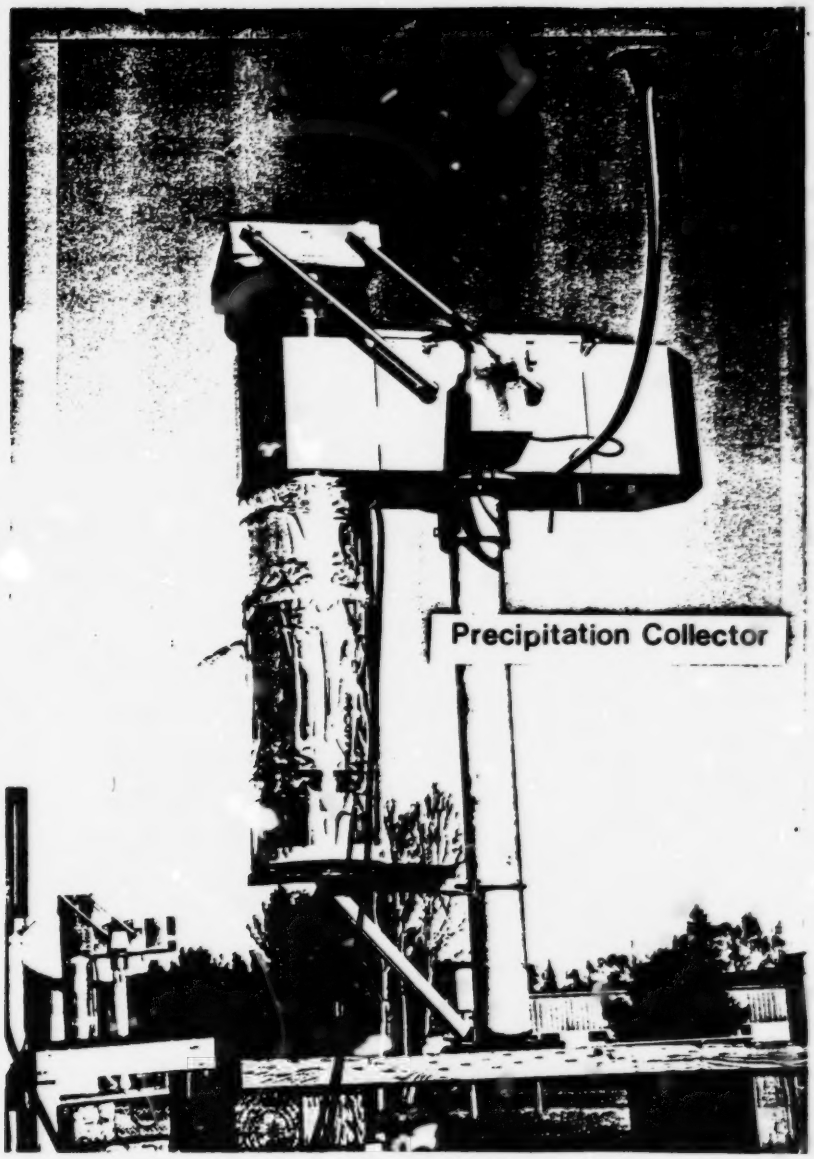

Figure 2: The APIOS precipitation collector

Figure 3: The APIOS low-volume air sampler

3. PRECIPITATION ACIDITY

The acidity of precipitation is usually expressed in terms of the pH parameter, which is the negative of the logarithm of the hydrogen ion concentration. In very clean areas, the pH of precipitation is expected to be 5.6, due to dissolution of the slightly acidic carbon dioxide gas, which is ubiquitous. In polluted areas, precipitation acidity levels for individual rainfalls can be a hundred times higher (i.e., pH values as low as 3.6), mainly due to the incorporation of sulfuric and nitric acids, which are formed from sulfur dioxide and nitrogen oxide emissions.

Figure 4 shows the long-term pH values in Ontario, determined from data collected during four years (1981-1984). Note that in central and southern Ontario, the average precipitation pH is presently less than 4.3 (i.e. the acidity is more than 20 times that of "clean" rain). These are long-term average values. As was already pointed out, for individual events, the pH can fall considerably lower.

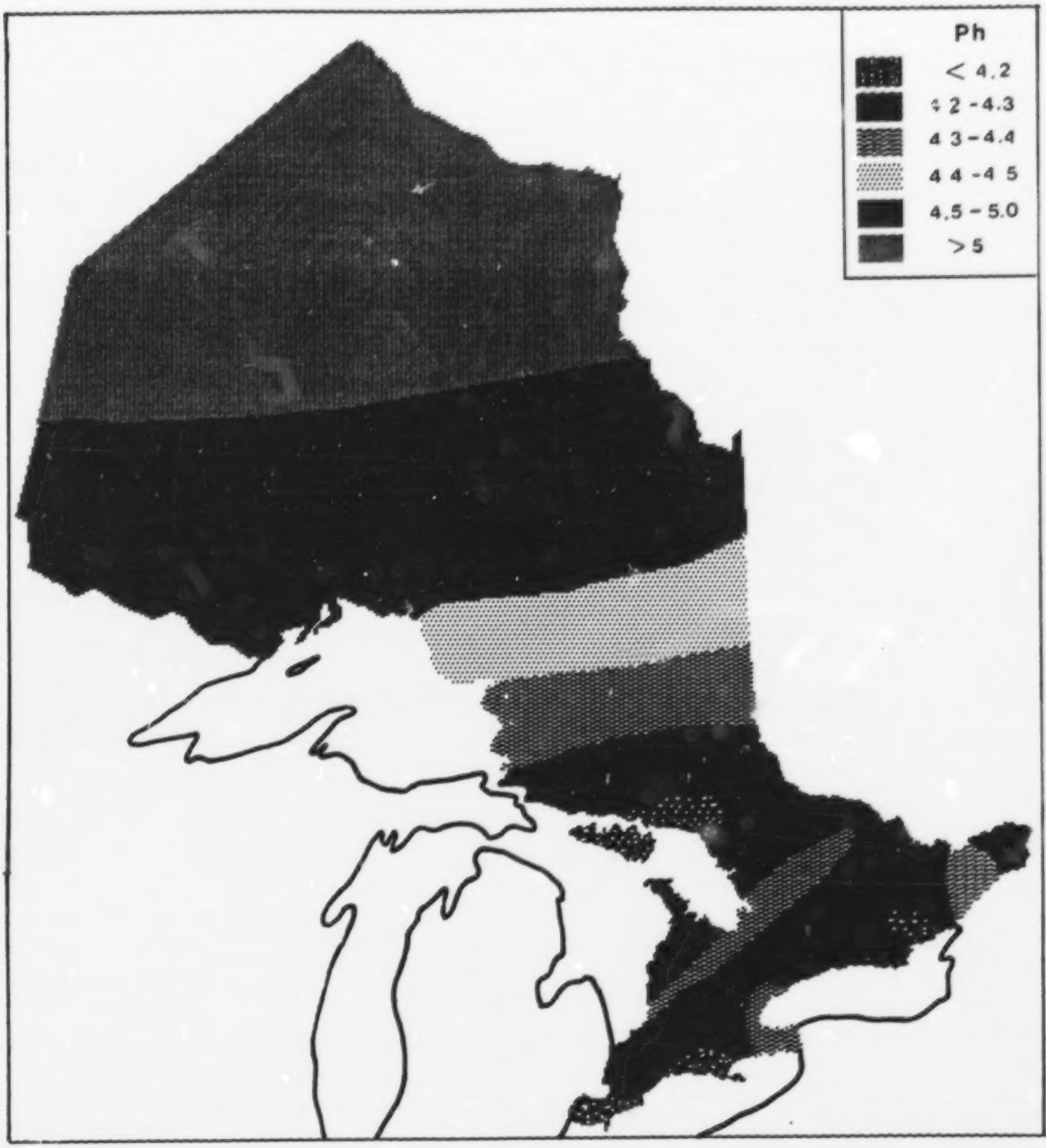

Figure 4: Precipitation pH

4. SULFATE WET AND DRY DEPOSITION

Much of the acidity in precipitation comes from sulfuric acid. Actually, many scientists now feel that the environmental impact of acid rain can be inferred from the rate of sulfate wet deposition. An annual rate of wet deposition greater than 20 kg sulfate per hectare is thought to be harmful to sensitive aquatic ecosystems (Very sensitive ecosystems may be affected by loading considerably less than this). As can be seen from Figure 5, this value is exceeded in all of central and southern Ontario. Figure 5 shows the annual sulfate wet deposition, determined from 1981-1984 data.

Acidifying sulfur oxides can also be delivered to the earth's surface by dry deposition processes - the direct absorption of sulfur dioxide gas from the atmosphere by water, soil and vegetation, and the impaction and gravitational settling of airborne sulfate particles. When these are taken up by the surface, the net result can be the same as when acid rain falls on the surface. Figure 6 shows the dry deposition rate of sulfur oxides, expressed in the same units as the wet deposition in Figure 5, i.e. as kilograms of sulfate per hectare per year. Note that dry deposition can deliver a significant additional loading of sulfur oxides, over and above that due to precipitation. In southern Ontario, the dry deposition of sulfur oxides is about one-half of the wet deposition rate. In central and northern Ontario, the dry deposition rate is about one-quarter or one-fifth of the wet deposition rate. The following table shows the total, and percent wet and dry, deposition rates of sulfur oxides in different regions of Ontario (the location of these regions can be found on the map in Figure 1(b).)

Region	Sulfur Oxide Deposition (as kg SO_4/ha/y) Total	Wet (%)	Dry (%)
Southwestern and West Central	53.8	67.4	32.6
Central	37.9	75.1	24.9
Southeastern	31.5	82.5	17.5
Northeastern	26.3	80.4	19.6
Northwestern	9.1	82.5	17.5

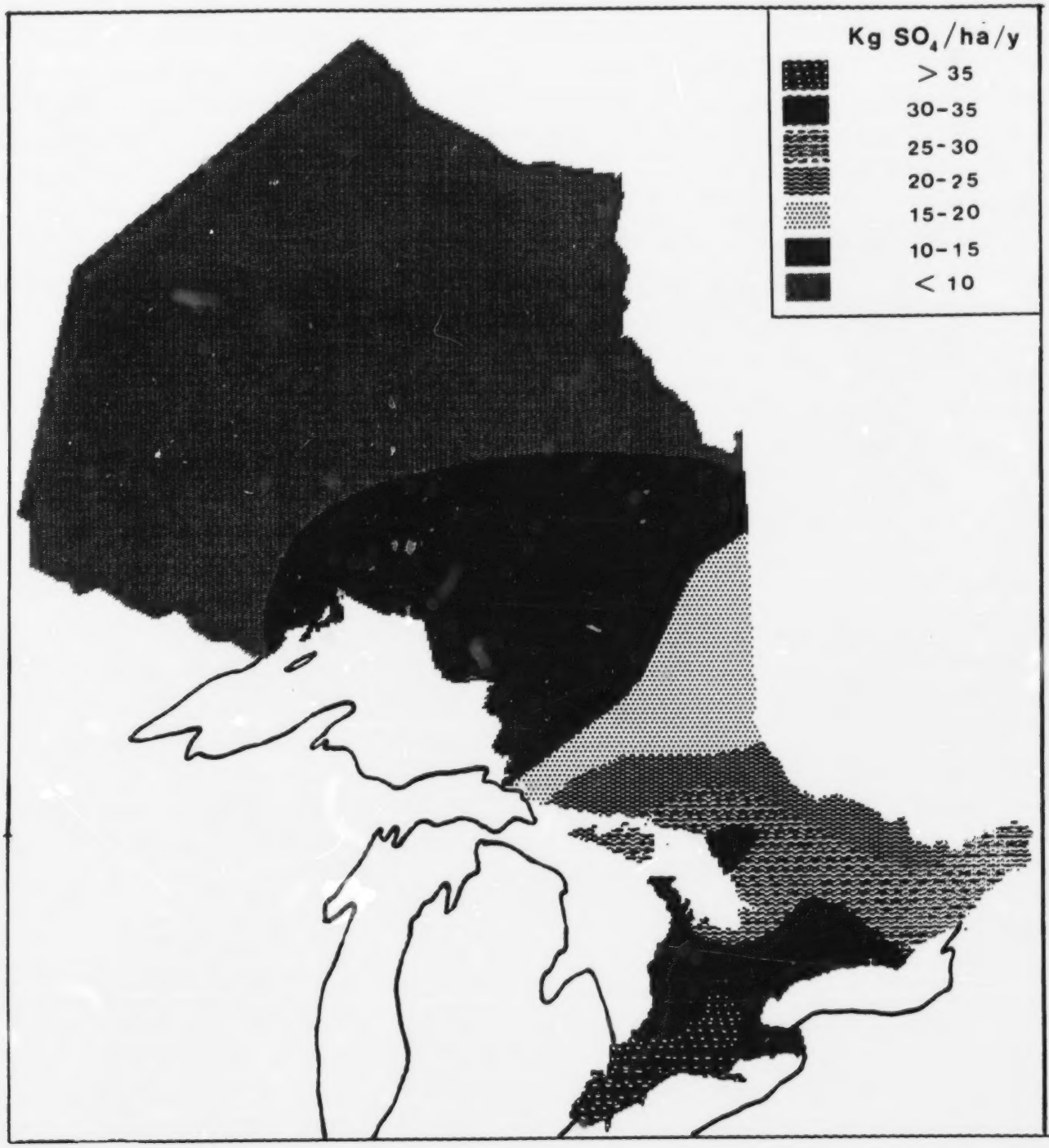

Figure 5: Sulfate wet deposition (kg/ha/y)

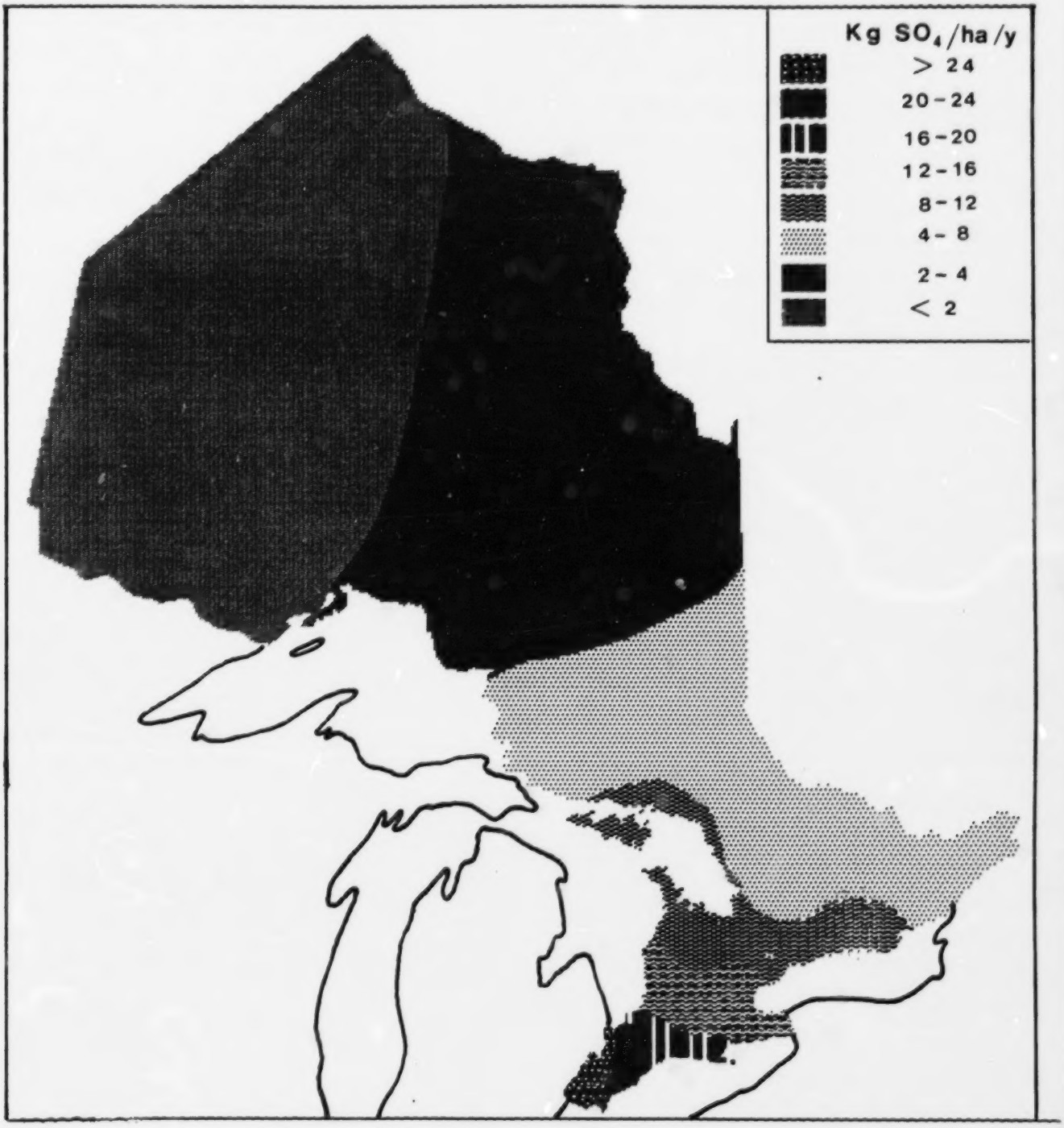

Figure 6: Sulfate dry deposition (kg/ha/y)

Figures 5 and 6 also reveal that the atmospheric deposition of sulfur oxides is much greater in southern Ontario, near the emission source areas along the Great Lakes and in the heavily industrialized states to the south of the Great Lakes. This deposition pattern clearly illustrates the impact of man-made emissions.

5. NITRATE WET AND DRY DEPOSITION

The other major contributor to precipitation acidity in Ontario is nitric acid. Figure 7 shows the nitrate wet deposition rate determined from 1981-1984 data, and expressed as kg nitrogen per hectare per year. Figure 8 shows the estimated annual dry deposition rate for nitrates. A comparison of these figures shows that the wet and dry deposition rates are similar across the province. This is so because a large portion of the airborne nitrogen oxides is in the form of nitric acid, which is very readily absorbed by surfaces, hence giving a high dry deposition rate.

As with sulfur oxides, there is a rapid drop-off of atmospheric deposition with increasing distance from the emission areas in the northeastern United States and southern Ontario. The table below illustrates (using 1981-1984 data) how the total annual nitrate deposition, and the contribution from wet and dry processes, varies in the different regions of the province.

Region	Nitrate Deposition (as kg N/ha/y) Total	Wet (%)	Dry (%)
Southwestern and West Central	8.61	59.9	40.1
Central	7.61	59.9	40.1
Southeastern	6.59	60.2	39.8
Northeastern	5.16	59.3	40.7
Northwestern	2.01	67.7	32.3

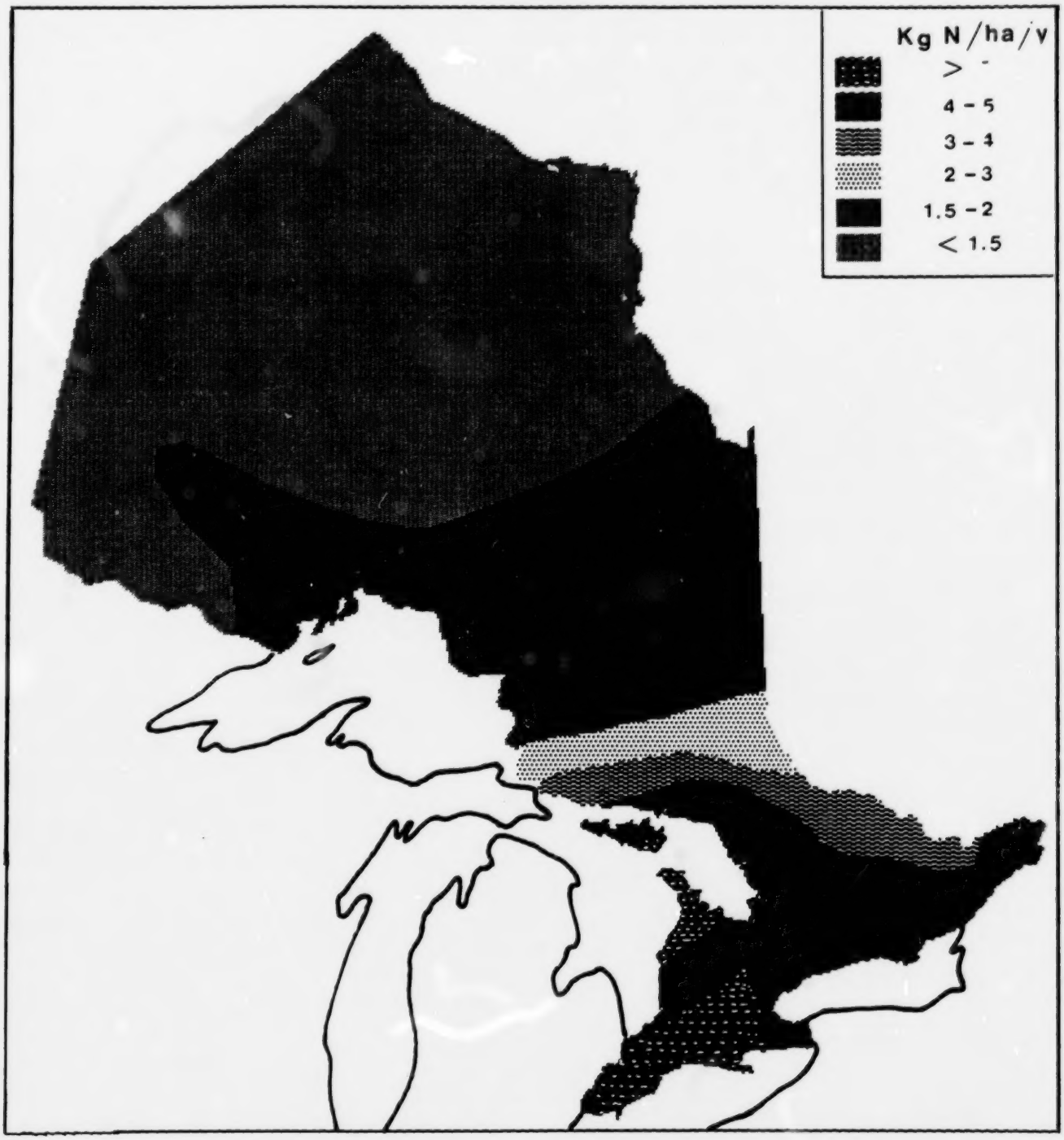

Figure 7: Nitrate wet deposition (kg/ha/y)

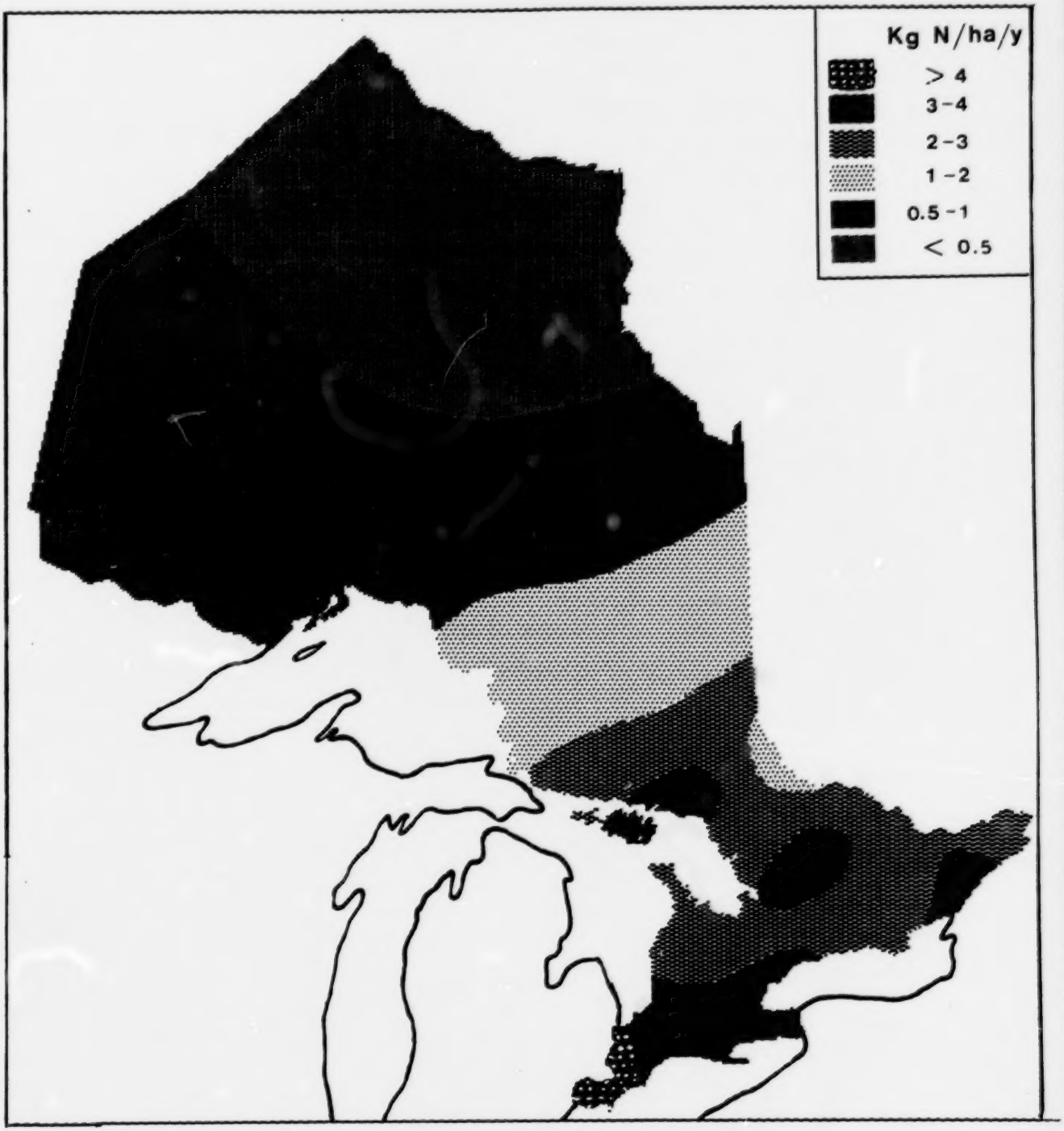

Figure 8: Nitrate dry deposition (expressed as kg N/ha/y)

6. SULFATES VERSUS NITRATES IN ACID DEPOSITION

Figures 5-8 may give a misleading impression regarding the relative deposition of acidity due to nitrates and sulfates, because of the different units used to express the results. To express the impact of sulfates and nitrates on a comparable basis, the values shown in these figures can be converted to "equivalent weights". On this basis, each equivalent weight of sulfate has the potential of yielding the same amount of acidity as an equivalent weight of nitrate.

When the atmospheric deposition (wet plus dry) results are converted to equivalent weights of sulfates and nitrates, it is found that their potential for environmental acidification is comparable, i.e. almost as much acidity is due to nitrogen as sulfur oxides. This is illustrated in the table below, which shows the total deposition (wet plus dry) of sulfur and nitrogen oxides in different regions of the province, in terms of equivalents per hectare per year, as well as the percentage due to sulfur and nitrogen compounds. Clearly, although the total atmospheric deposition of acid-related compound drops sharply going from south to north, the relative contribution of sulfur and nitrogen compounds remains similar, about 56-60% of the acidifying potential coming from the sulfur oxides.

Sulfur and Nitrogen Oxide Deposition
(as equivalents/ha/y)

Region	Total	S (%)	N(%)
Southwestern and West Central	1.74	56.3	43.7
Central	1.33	59.2	40.8
Southeastern	1.13	58.2	41.8
Northeastern	0.92	59.7	40.3
Northwestern	0.33	57.0	43.0

7. SEASONAL TRENDS

Atmospheric deposition can change from season to season, since it is determined by the amount and nature of the precipitation, the stability of the atmosphere (which can be quite different for winter and summer months), the state of the surface on which dry deposition processes partly depend, and the rate of atmospheric chemical reactions (which depend on the time of year). Figures 9 and 10 show how the atmospheric deposition of sulfur and nitrogen oxides varies with the season at the APIOS Dorset monitoring station, near Algonquin Park. The results here, for 1981 to 1984, are representative of other sites in central and southern Ontario as well.

Note that for sulfates, a maximum in the atmospheric depositon occurs during the summer months. For nitrates, there is a moderate increase of the deposition in the winter. When expressed in terms of equivalent weights, the amount of acidity potentially delivered by nitrates during the winter season is about twice as great as that delivered by sulfates. This findings emphasizes the importance of nitrogen oxide emission controls. The acidity accumulated in the snow pack during the winter months can lead to "acid shock", and result in damage to aquatic ecosystems, on arrival of the spring melt season.

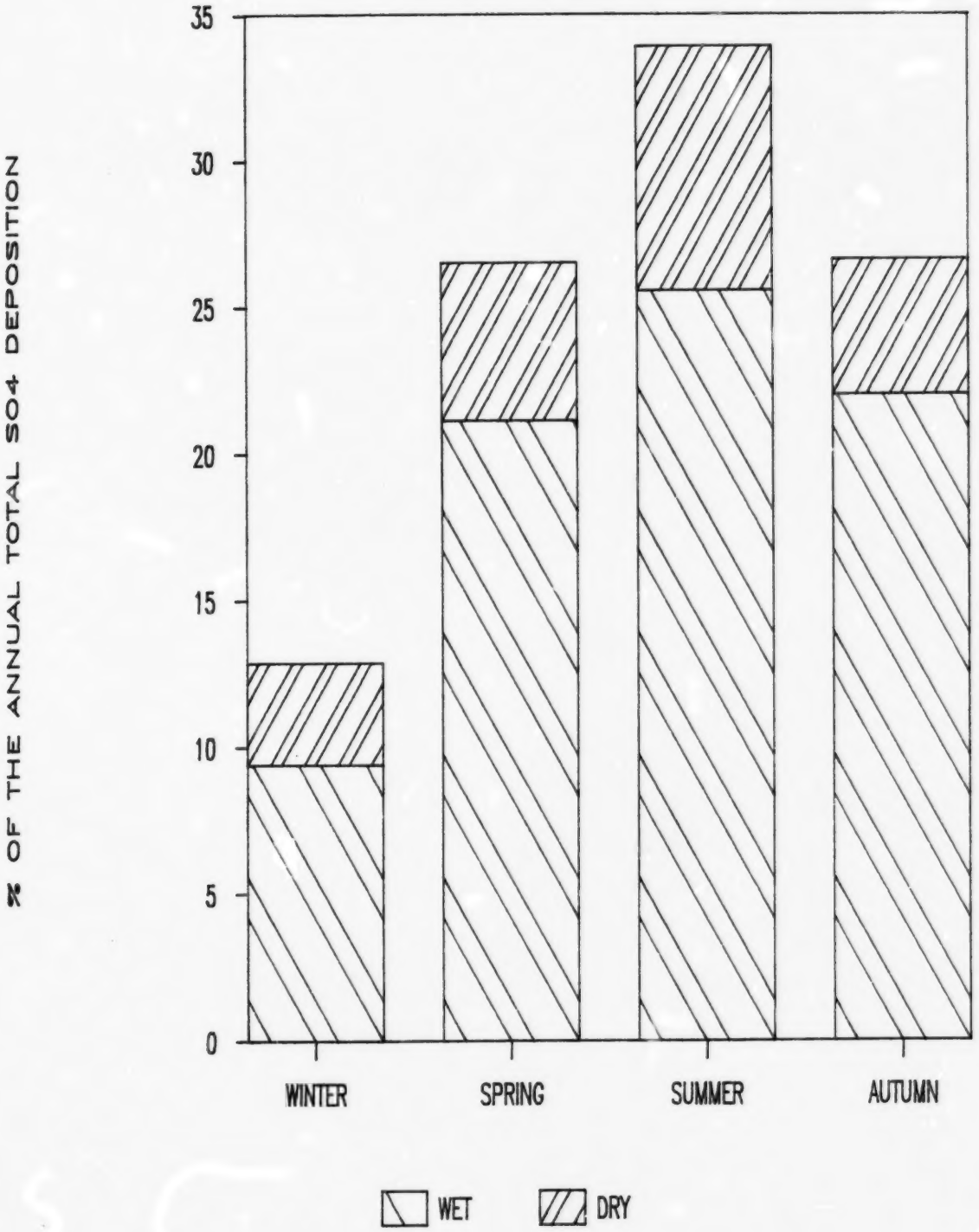

Figure 9: Seasonal variations of the atmospheric deposition of sulfur oxides.

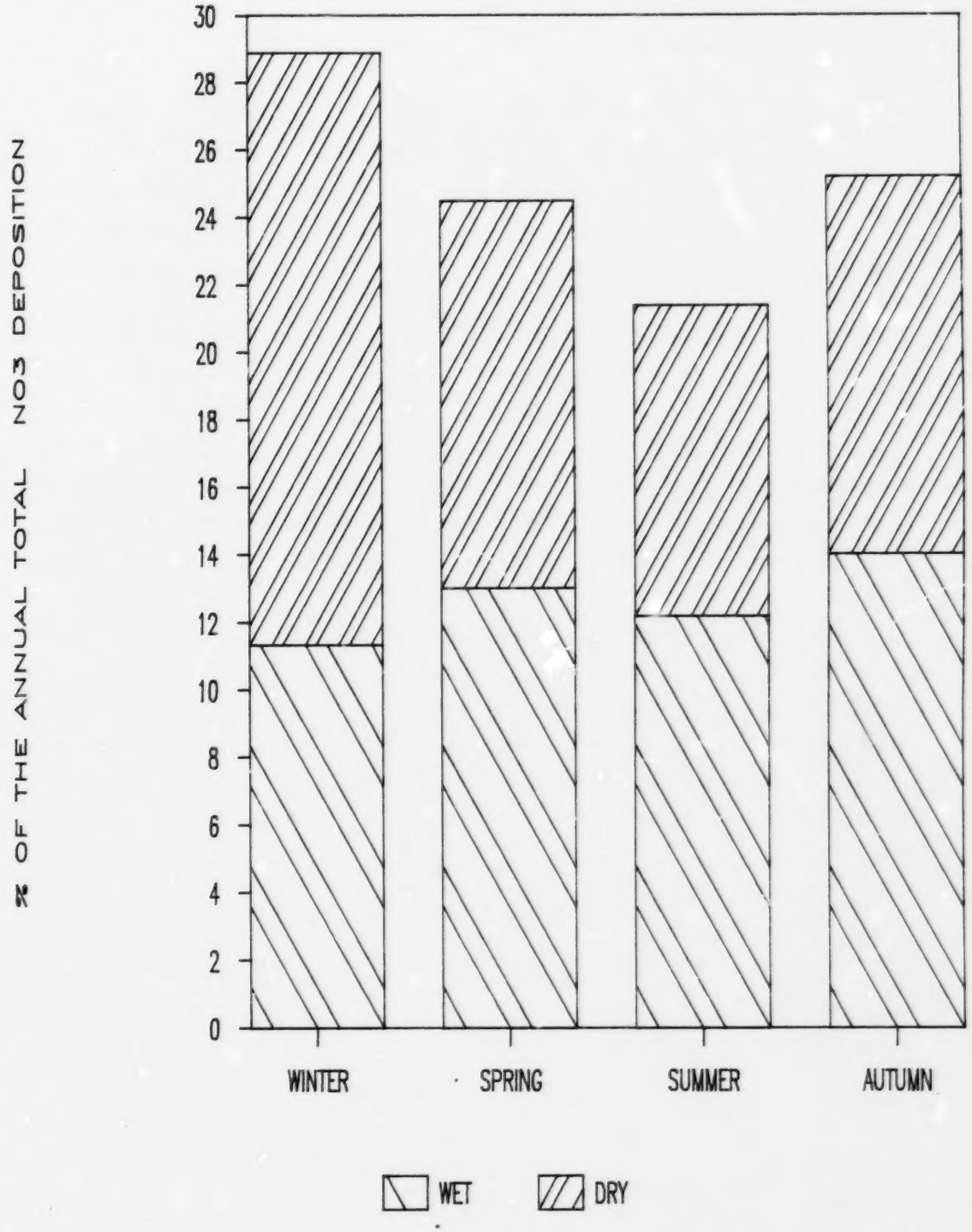

Figure 10: Seasonal variations of the atmospheric deposition of nitrates

8. ANNUAL TRENDS

The amount of atmospheric deposition varies from year to year, because of changes in emission rates or meteorological variability, for example. As everyone knows, there can be large changes in the amount of precipitation at a given location from one year to the next, and the wet deposition rate depends strongly on this factor.

Figure 11 shows how the annual atmospheric deposition of sulfates at Dorset has varied during the 1981-1984 period. Note that even when expressed on an annual average basis, there can be a considerable year-to-year variation in the atmospheric deposition (the seasonal or individual event variability is of course much greater). During the four-year period shown in Figure 11, the annual sulfate wet deposition values have fluctuated between about 24 and 35 kg/ha/y. Corresponding values for nitrate are shown in Figure 12. Such year-to-year variability is largely due to meteorological factors, and makes it difficult to isolate the effects of emission controls (such as Ontario's "Countdown Acid Rain" program) on acid deposition. However, by accumulating a sufficiently long data record, and by applying special data analysis techniques, the benefits of emission controls can be determined. Our network is closely monitoring the results of Ontario's emissions control program.

The values for sulfate dry deposition in Figure 11 include the contribution of sulfur dioxide and sulfate particulates: those for nitrate in Figure 12 include the contribution of nitric acid vapour and nitrate particulates. The nitrate deposition results are expressed in terms of kg N/ha/y: those for sulfate, are expressed as kg SO_4/ha/y.

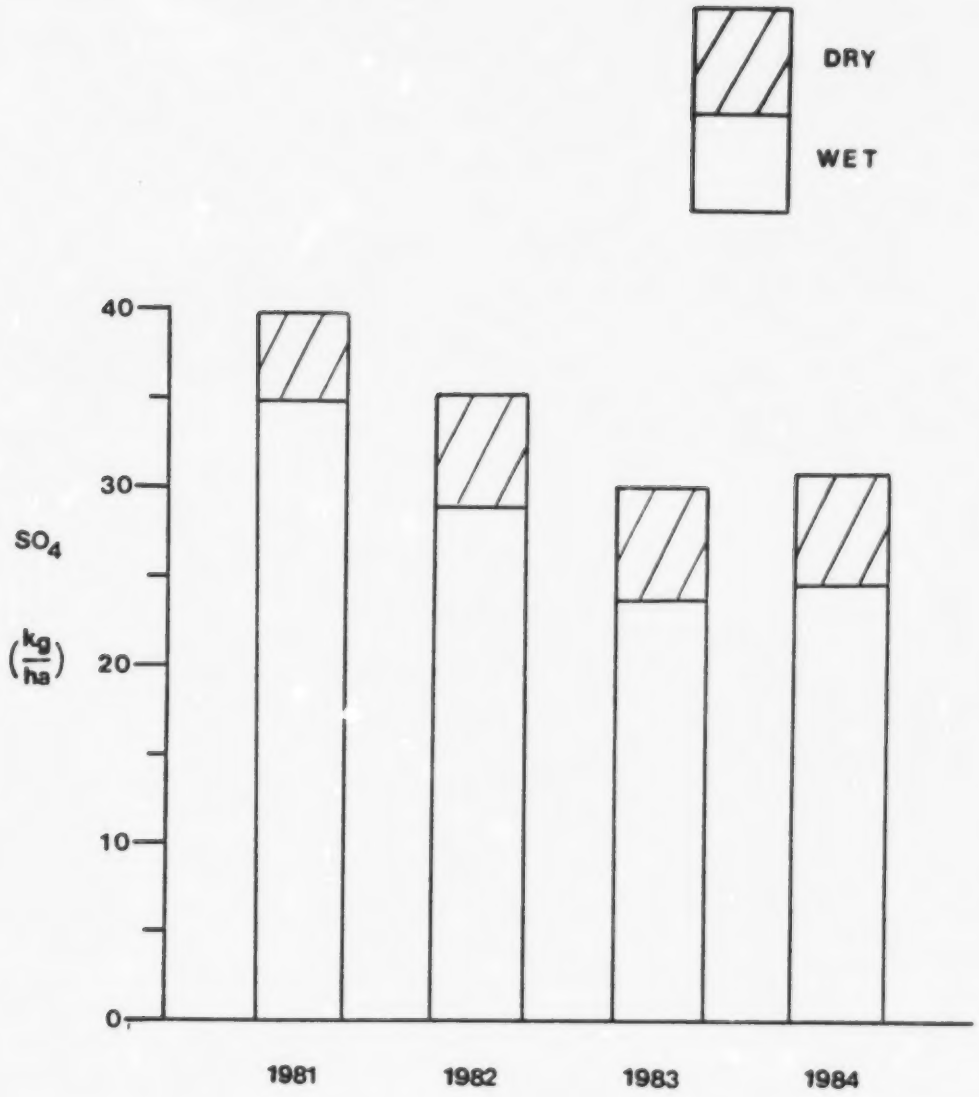

Figure 11: Variation of annual sulfate deposition (expressed as kg SO_4/ha) during the 1981-1984 period.

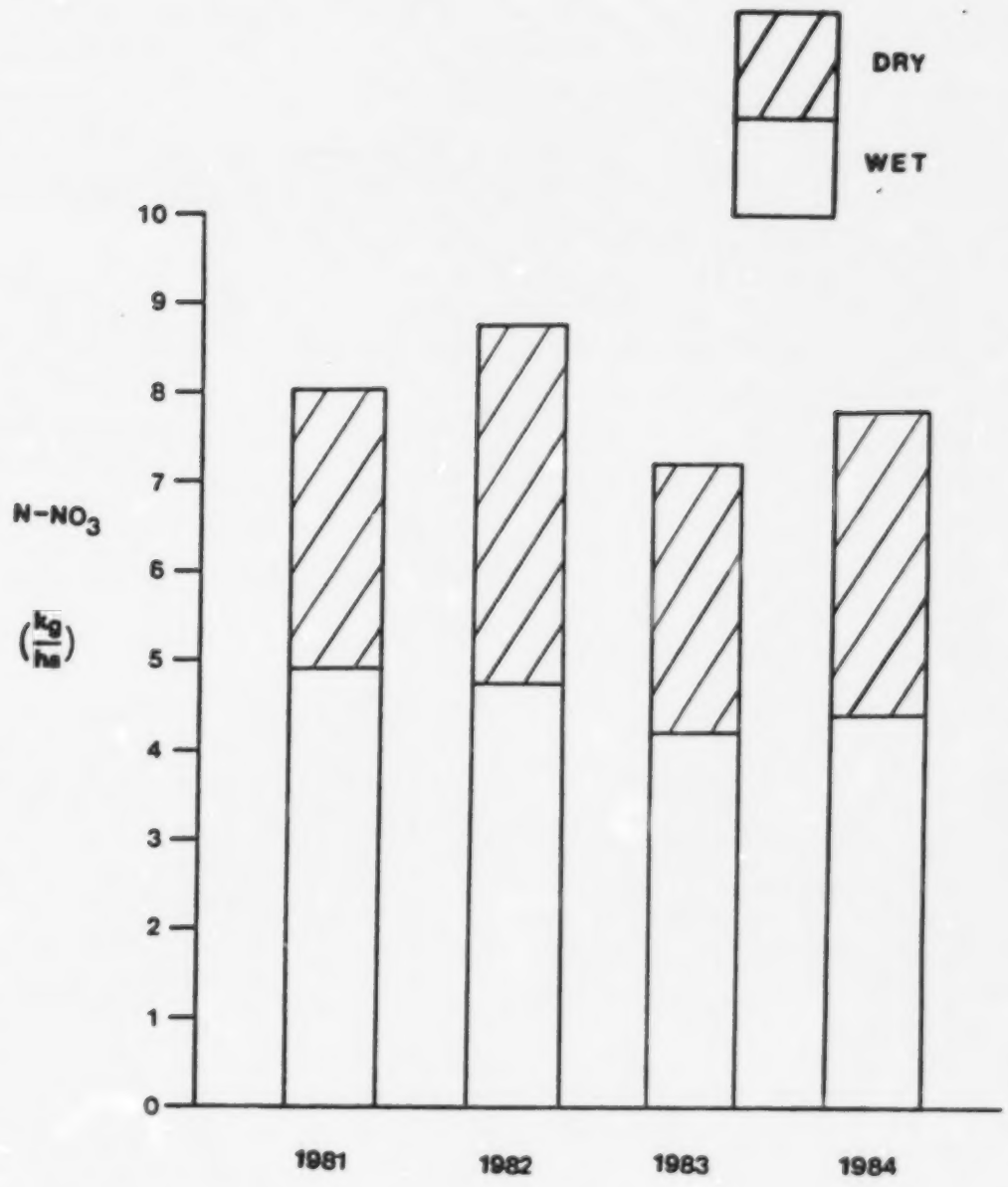

Figure 12: Variation of annual nitrate deposition (expressed as kg N/ha) during the 1981-1984 period.

9. ATMOSPHERIC DEPOSITION OF OTHER TOXIC SUBSTANCES - LEAD AND CADMIUM

As was mentioned in Section 2, the APIOS network also monitors the levels of various toxic trace metals. Among them, lead and cadmium are of particular current interest, especially with respect to their atmospheric deposition to the Great Lakes basin. Deposition from the atmosphere is thought to be the major source of these metals in water from the Great Lakes. The results on annual wet and dry deposition rates of lead and cadmium in Ontario (based on 1981-84 data) are given in Figures 13-16. As with the sulfur and nitrogen compounds, deposition is greatest in the southern parts of the province near the heavily populated and industrialized areas of Ontario and the northeastern United States.

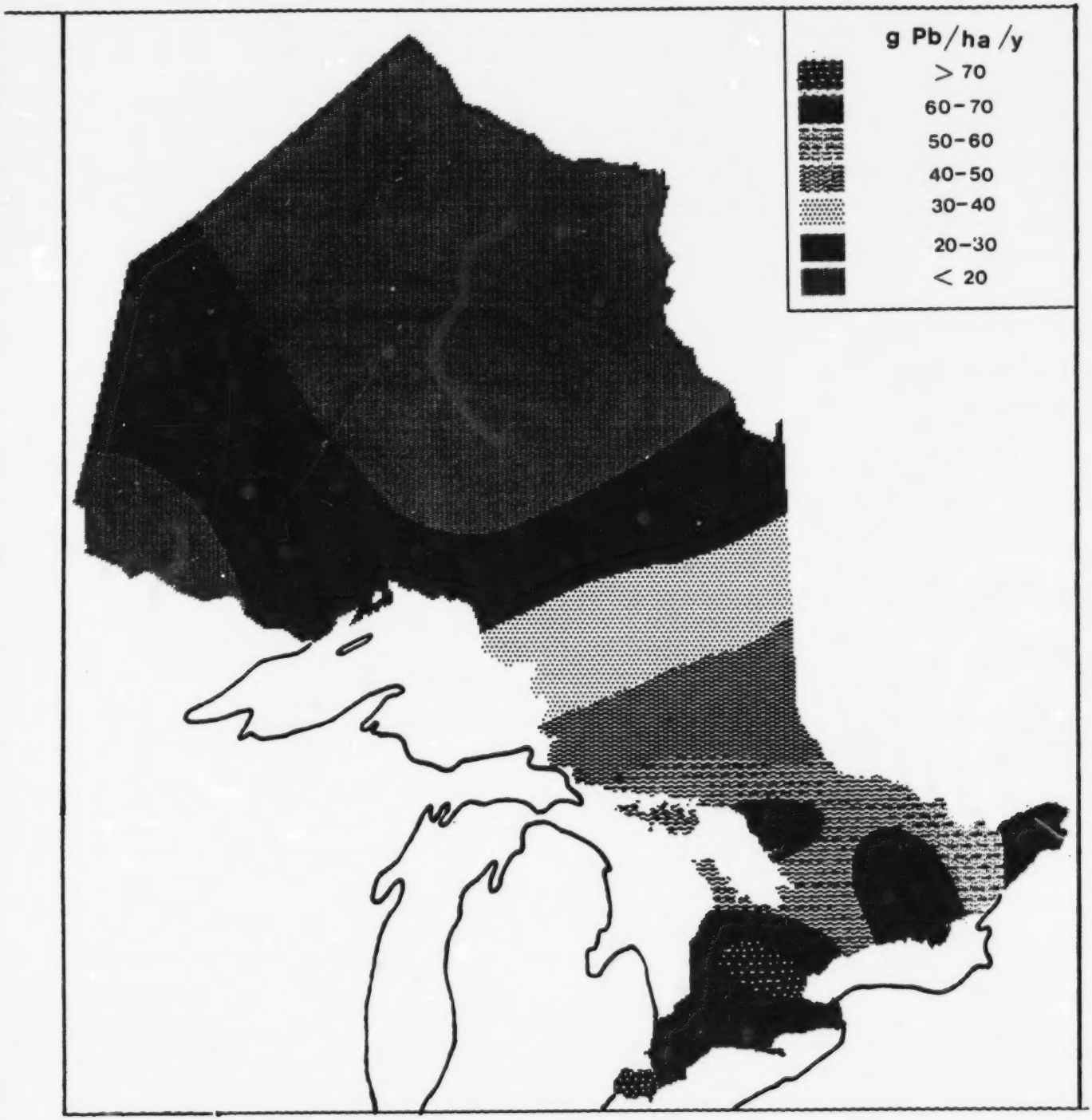

Figure 13: Wet deposition of lead (g/ha/y) based on 1981-1984 data

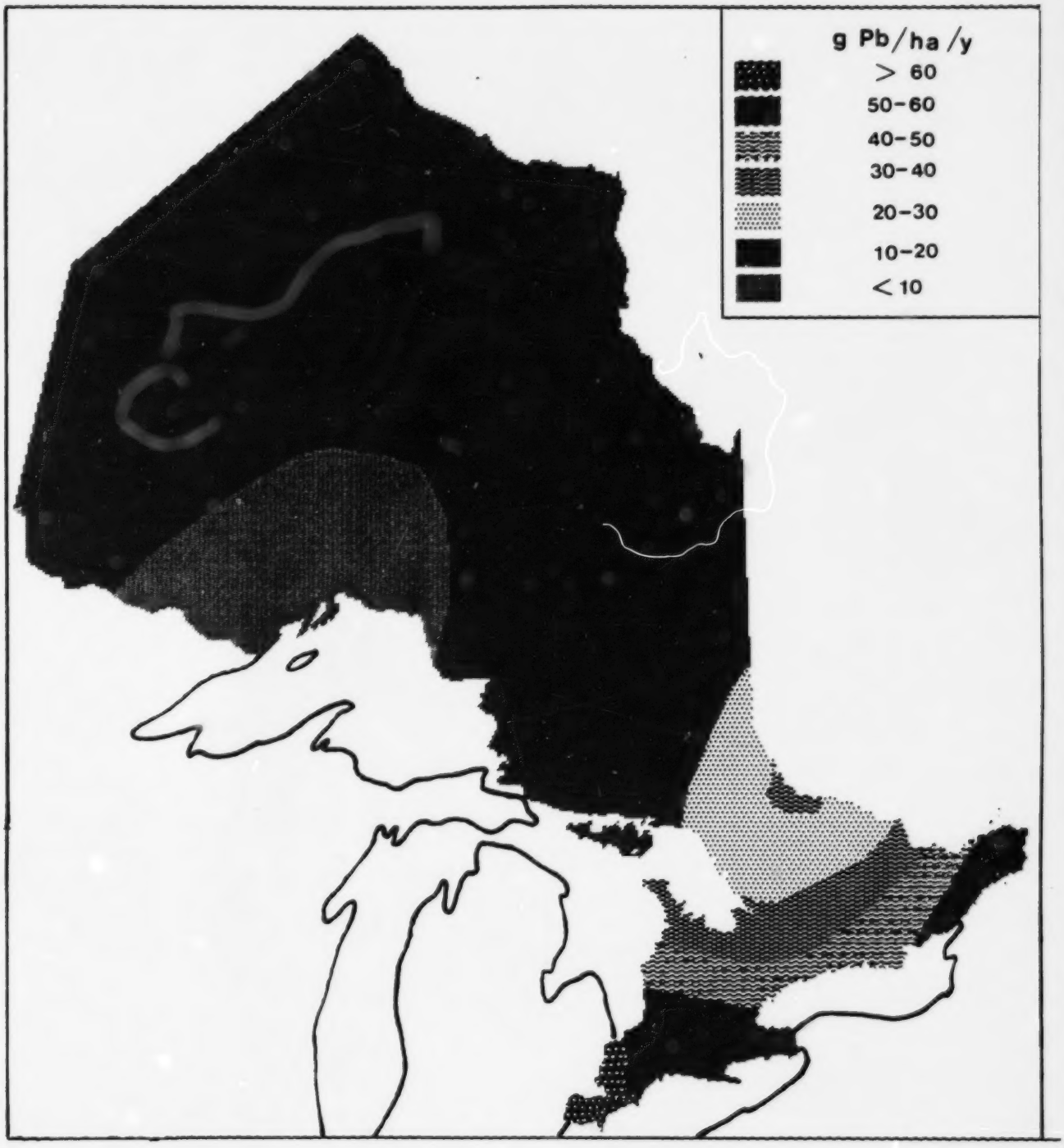

Figure 14: Dry deposition of lead (g/ha/y) based on 1981-1984 data.

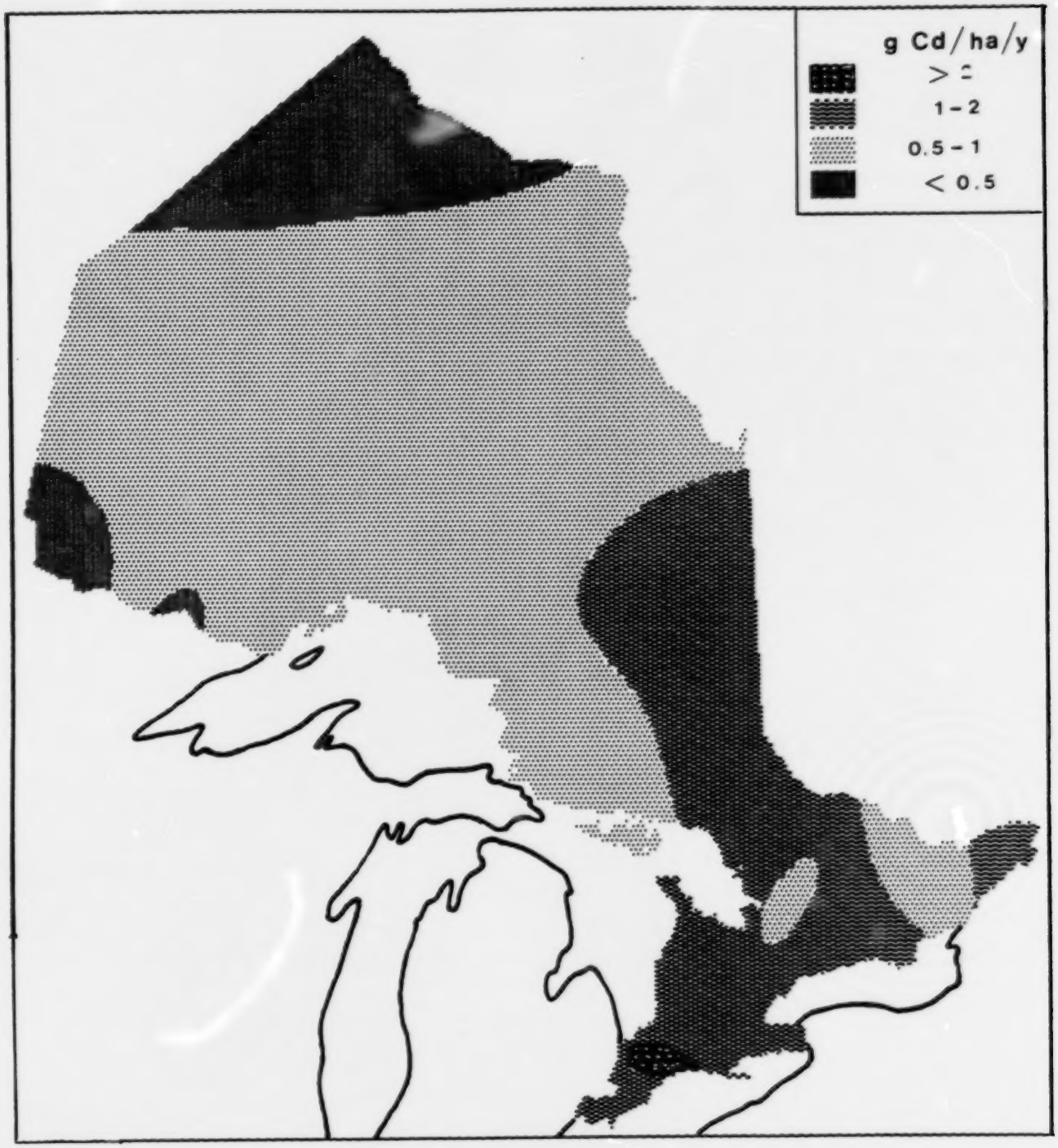

Figure 15: Wet deposition of cadmium (g/ha/y) based on 1981-1984 data.

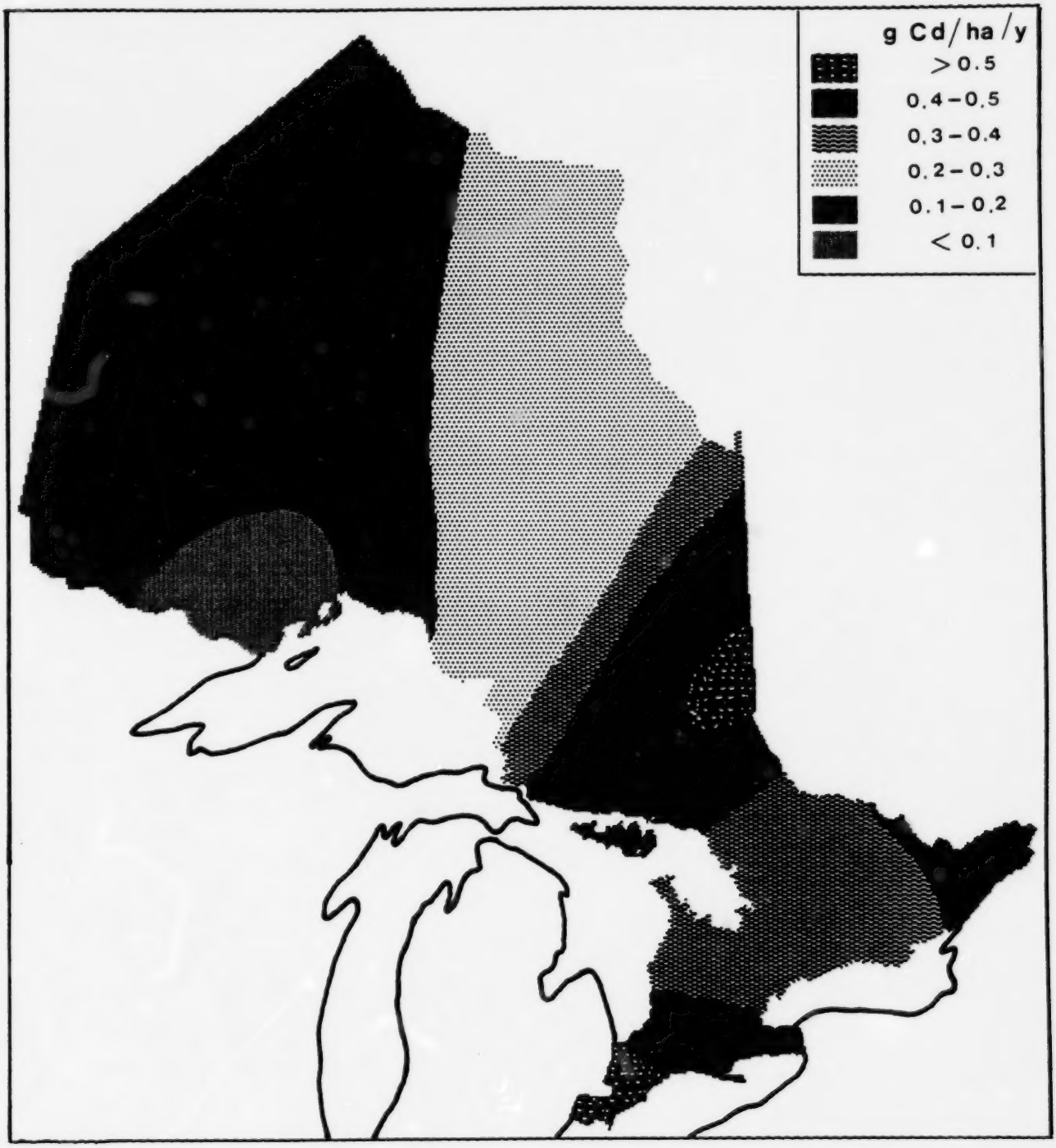

Figure 16: Dry deposition of cadmium (g/ha/y) based on 1981-1984 data.

10. CONTRIBUTION OF DIFFERENT EMISSION SOURCES TO ATMOSPHERIC DEPOSITION IN ONTARIO

The question, "How much does an emission source area (e.g. the states south of the Great Lakes) contribute to a particular receptor area (e.g. Algonquin Park)?" is of considerable interest to the acid rain problem. We now know that the sulfur and nitrogen oxides which cause acidic deposition can travel for hundreds of kilometres from their points of emission, before being deposited on the earth's surface through wet and dry processes. The control of the acid rain problem will thus require both regional and local emission reductions. Ontario has already committed itself to a 50% reduction of sulfur dioxide emissions by 1994 (compared to 1980 as the base year). What effect is this reduction expected to have on acid rain in Ontario, if nothing is concurrently done to control the large emission sources south of the Great Lakes in the United States?

One way to answer this question is by the use of mathematical models, which simulate the long-range transport, and atmospheric chemical transformation and deposition, of sulfur and nitrogen oxides. However, because of the complexity of atmospheric processes, many scientists feel that the current generation of long-range transport models does not represent these processes sufficiently, to give an accurate answer. More detailed models (called long-range transport eulerian models) are presently being developed. In the meantime, some useful answers can be obtained from a careful meteorological analysis of the monitoring data, especially data collected for individual events.

Several such analyses have been carried out by the Ministry's scientists. The contribution of Canadian and United States sources at some monitoring stations near the border has been assessed using air parcel trajectory analyses. By this technique, the geographical areas over which the air parcel has passed during the previous day or two can be determined, and thus the portion of the measured atmospheric deposition due to emissions from the sources within different compass sectors can be assessed. Figures 17 and 18 show the results of such an analysis at Longwoods and Railton, giving the percentage of the wet deposition of sulfates and nitrates due to USA, and Canadian sources. Although the results from border stations are particularily easy to interpret, since there is a clear-cut distinction between USA and Canadian source sectors, some air

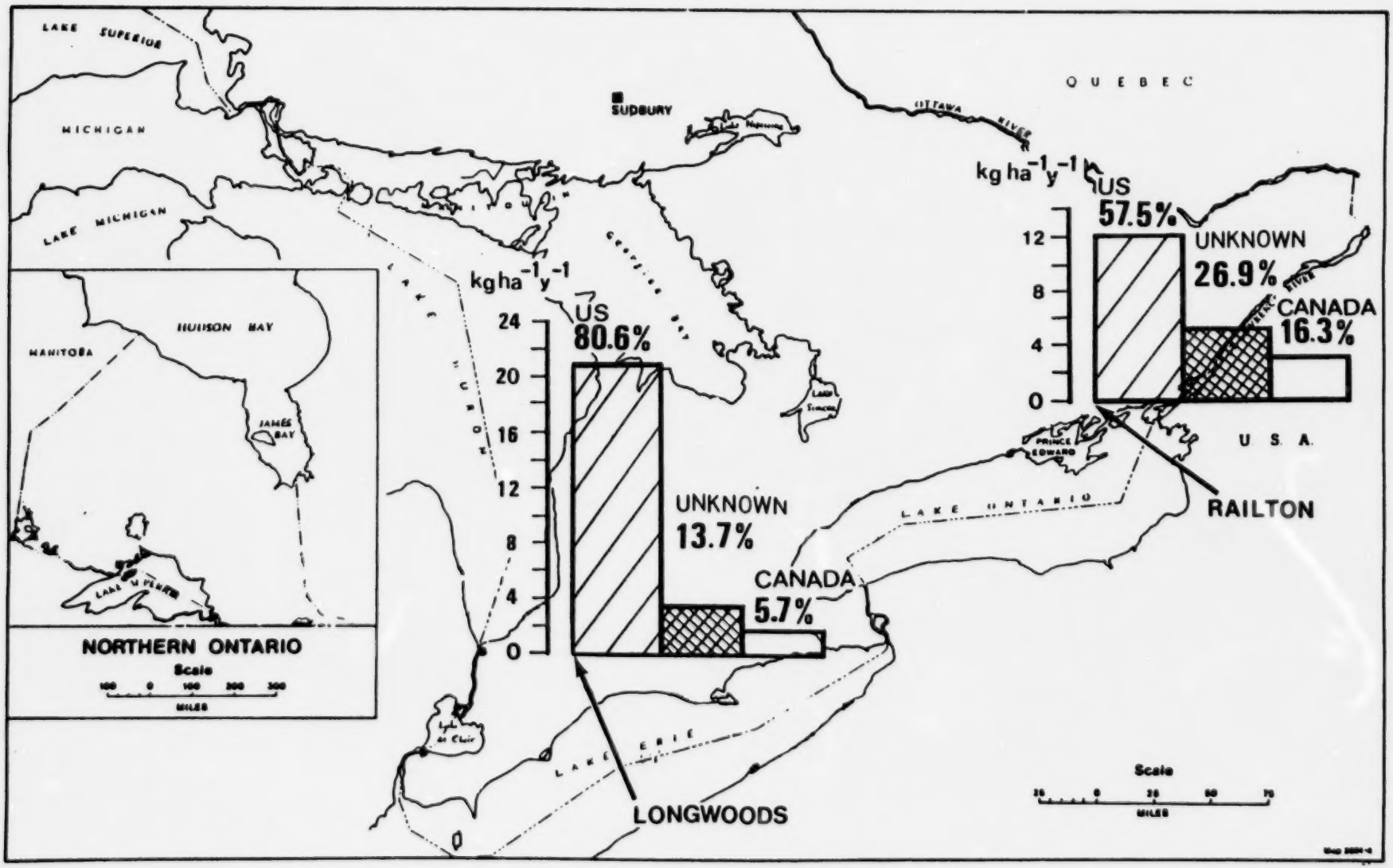

Figure 17: Apportionment of sulfate wet deposition sources at Longwoods and Railton, using 1981-1983 data (the scale is in kg SO_4/ha/y)

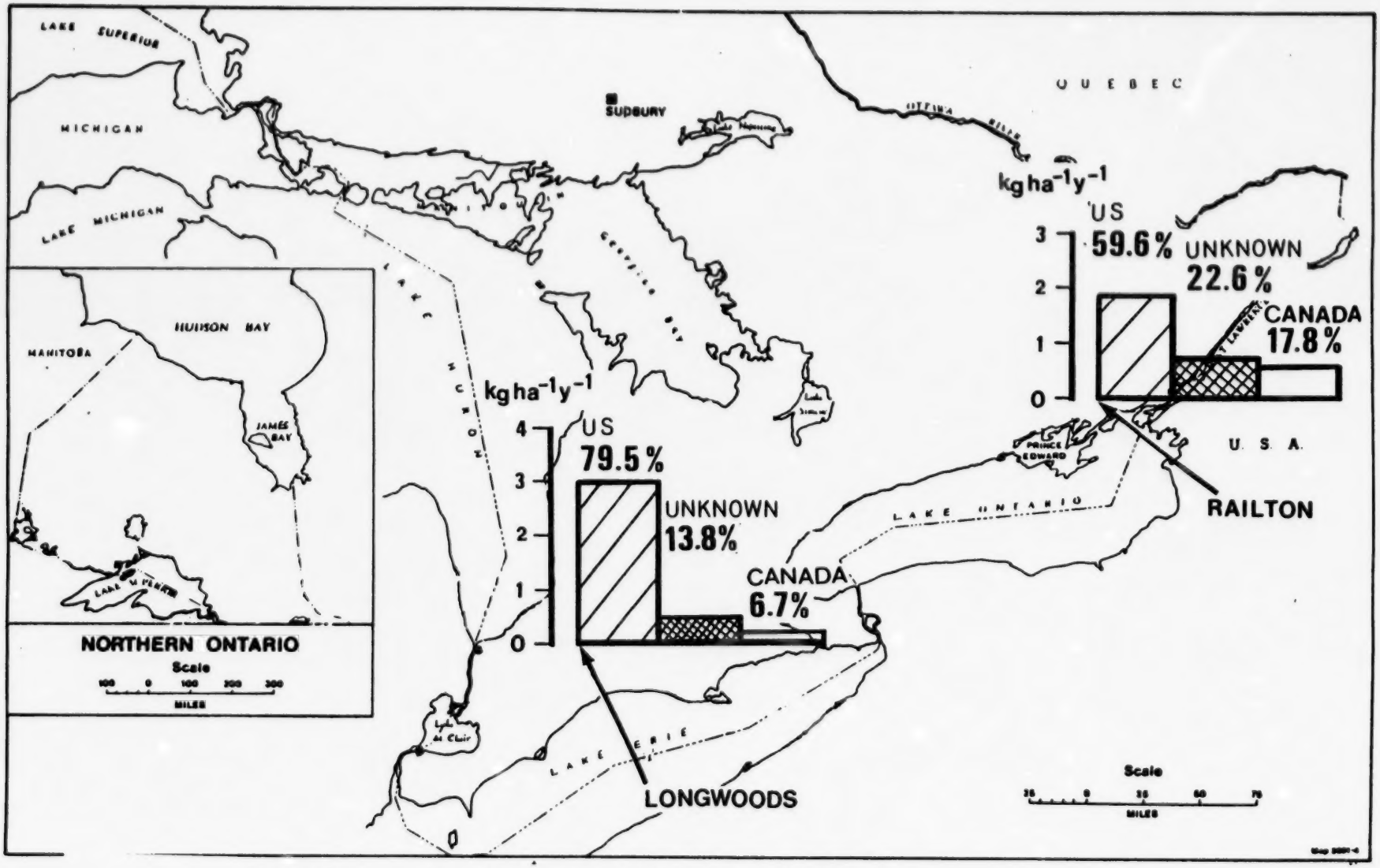

Figure 18: Apportionment of nitrate wet deposition sources at Longwoods and Railton, using 1981-1983 data (the scale is in kg N/ha/y).

parcel trajectories (about 14% at Longwoods and 23-27% at Railton) still traverse both U.S. and Canadian areas during two days of travel, and are placed in the "unknown" category. Nevertheless, Figure 17 and 18 indicate that at least 80% of the sulfate and nitrate wet deposition in southwestern Ontario, and about 60% in southeastern Ontario, is due to emissions in the United States. This result is not surprising. Southwestern Ontario, for example, forms a wedge extending into a heavily industrialized area of the United States. Within two days of air parcel travel time of Longwoods, the United States sector contains emission sources of about 16 million tonnes of SO_2 per year: the Canadian sector contains sources totalling only about 1.5 million tonnes. Thus the results of our source apportionment analysis are consistent with the emissions information, and our knowledge of the residence time of sulfur oxides in the atmosphere. It should be noted that by the above analysis, we cannot distinguish between the atmospheric deposition due to anthropogenic and natural sources. If the contribution due to natural sources (based on the best information currently available to us) is subtracted away from the anthropogenic contribution, then the percentages in Figures 17 and 18 will change somewhat.

The results of another analysis tell a similar story. This analysis considered the impact of two large sources in Ontario - the INCO and Falconbridge smelters at Sudbury - on wet and dry deposition at various locations. Together, these sources contributed about one-half of the total annual sulfur dioxide emissions in the province in 1980. However, during a prolonged shutdown of the smelters in 1982-1983, it was difficult to detect any decrease in the atmospheric deposition of sulfur oxides. A variety of meteorological analysis techniques were used. Figure 19 shows the results. The numbers in the triangles are the estimated smelter contributions (% of the annual total) sulfate wet deposition at various receptors. The contribution was too small to be accurately quantifiable: it is expected to be "less than" the value shown in the triangle. Most of the sulfur dry deposition comes from sulfur dioxide, and the numbers in the boxes represent the smelter contribution to the sulfur dioxide dry deposition, determined by two different types of analyses. One, a simple trajectory analysis, allowed direct estimation of the smelter contibution: the other, involving a more detailed meteorological analysis, gave upper limits only (indicated by the "less-than" values).

The implications of the above results are clear: the largest sulfur dioxide emission source area in the province, Sudbury, contributes a relatively small

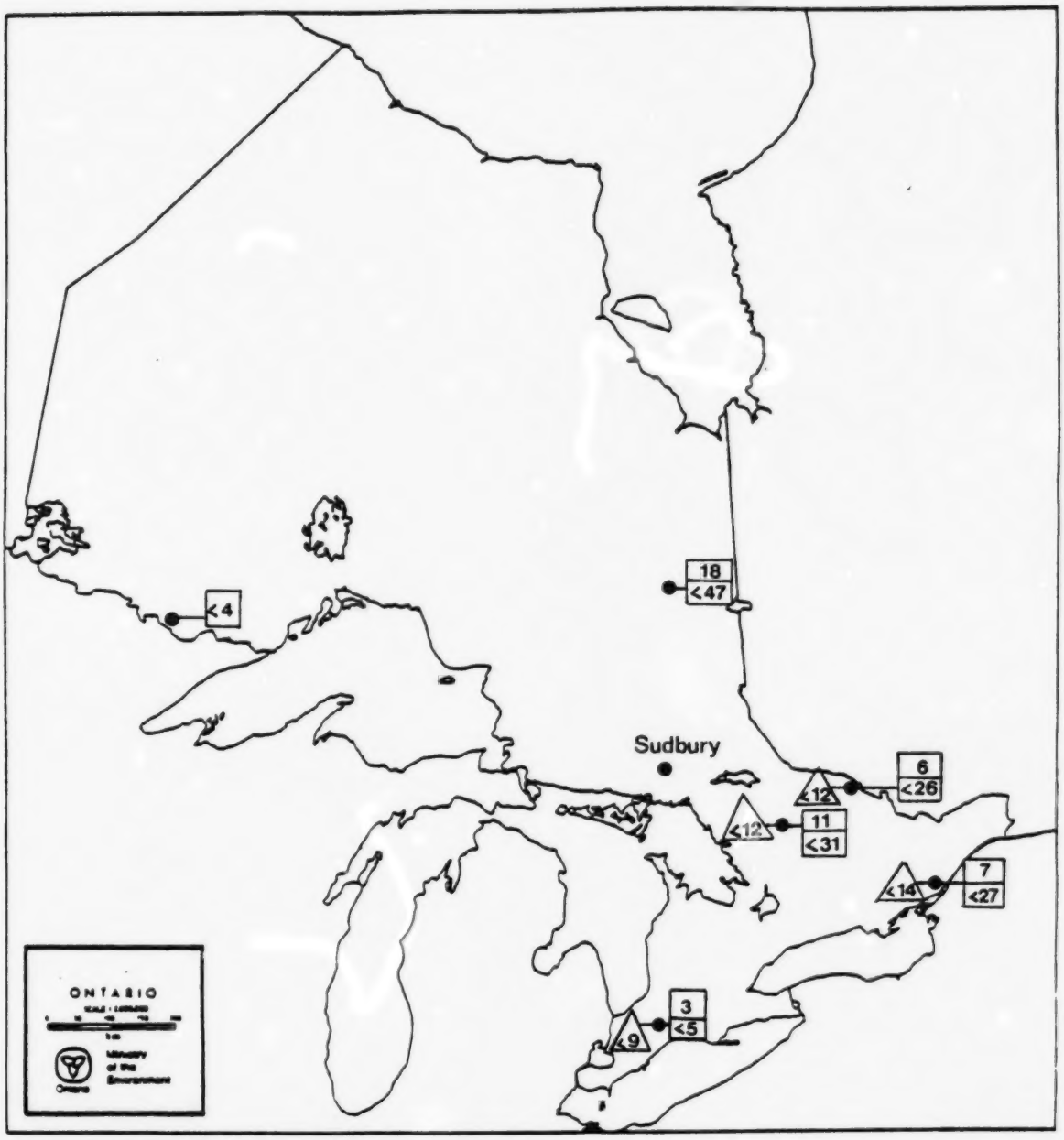

Figure 19: Contribution of Sudbury smelters (% of the annual total) to the wet and dry deposition of sulfur oxides in Ontario (wet deposition in triangles, dry deposition in boxes).

portion of the total atmospheric deposition of sulfur oxides (less than 14% of the total for wet, and about 40% or less for dry deposition). Therefore, the control of Ontario sources alone will not solve the acid problem. Without substantial emission reductions in the United States, acid deposition over large portions of the province will continue at unacceptable levels.

APS8/1